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RADIATIVE ENERGY TRANSFER ON ENTRY
INTO MARS AND VENUS

UNPUBLISHED PRELIMINARY DATA

IITRI-T200-7
(Quarterly Report No. 7)

RADIATIVE ENERGY TRANSFER ON ENTRY
INTO MARS AND VENUS

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FOREWORD

This report was prepared by the IIT Research Institute, Chicago, Illinois, for NASA Contract NASr-65(01). The contract is monitored by Dr. D. Easter of the Lunar and Planetary Exploration Branch, NASA Headquarters, Washington, D.C. The purpose of this program is to provide high temperature properties of simulated atmospheres of Mars and Venus. The present research program includes a measurement of the high temperature emissivity of N_2-CO_2 atmospheres and constituents of these atmospheres, and a measurement of the reaction rates that control the approach to equilibrium behind shock waves in these atmospheres. In this report the dissociation rate of CO_2 for temperatures of 6000°K to 11,000°K is presented. The principal investigator at IIT Research Institute is Mr. William O. Davies. Mr. David A. Gast has assisted in the research, and Dr. S. W. Kash has contributed helpful discussions and suggestions.

Respectfully submitted,

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ii

ABSTRACT

The dissociation rate of CO_2 has been measured for temperatures of 6000°K to 11,000°K. The rate of disappearance of CO_2 behind shock waves in a CO_2-Ar gas mixture was monitored by observing the infrared radiation from the CO_2 2.7μ combination bands. The dissociation rates expressed in the classical collision theory and an Arrhenius equation (in cm^3/particles-sec) are, respectively

$$k = (8.95)(10^{-13})(D/kT)^{3.21} \exp(-D/kT)$$

$$k = (1.92)(10^{-13}) T^{\frac{1}{2}} \exp(-2.96 \text{ eV}/kT)$$

where D = 5.5 eV is the CO_2 dissociation energy, k is the Boltzmann constant, and T is the absolute temperature. A rate constant was also determined from observations of emission at 3500 A, which is proportional to the product of the CO and O concentrations. The rates determined from these measurements are about a factor of three lower than those obtained from the infrared measurements, and the process has an activation energy of 3.68 eV as compared to the 2.96 eV for the infrared measurements. These results suggest that two different reactions are being observed; it is suggested that the infrared observations are a measure of CO_2 dissociation, while the UV emission is

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27302

controlled by the recombination of CO and O into an excited
state of CO_2, and the radiative life time of this CO_2 level.
The results obtained by both methods over a temperature range
of 2600°K to 10,000°K are summarized.

Author

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I.   INTRODUCTION

The results of an investigation of the thermal dissociation
of CO_2 at temperatures from 6000°K to 11,000°K are presented in
this report, and existing measurements of CO_2 dissociation for
temperatures from 2600°K to 11,000°K are summarized. In the
previous report[1] on this program the CO_2 dissociation rate was
given for dilute mixtures of CO_2 in both N_2 and Ar, for tempera-
tures from 3500°K to 6000°K. The rate of disappearance of CO_2
behind shock waves was monitored by observing the infrared
radiation from the CO_2 4.3 μ fundamental vibration band. The
dissociation rates for one percent CO_2 in Ar and N_2 were expressed
in terms of both the classical collision theory and an Arrhenius
equation, and it was found that these results were not altered
by (a) increasing the CO_2 concentration up to ten percent,
(b) adding either CO_2 or H_2O for concentrations of these gases
up to two percent, (c) making the dissociation measurement at
different wavelengths or pass bands within the 4.3 μ band, or
(d) making the dissociation measurement by observing radiation
from the 2.7 μ combination bands.

The results presented in this report are an extension
of the CO_2 dissociation measurements to higher temperatures,
with essentially the same experimental method as was used at
the lower temperatures. The high temperatures were obtained by

passing a shock wave through the test gas, which consisted of one percent CO_2 in Ar. The argon serves as a heat bath, permitting the attainment of high temperatures that are not significantly affected by the chemical reaction being observed. The pressure and temperature behind the shock wave were obtained from measurements of initial pressures and shock wave velocities. The rate of disappearance of CO_2 ($X'\Sigma$) behind the shock wave was determined by monitoring the CO_2 infrared radiation at 2.9μ, and, from a previous study of the emissivity of the 2.7μ CO_2 bands,[2] it is known that for the conditions of this experiment the CO_2 concentration is directly proportional to the intensity of the infrared emission.

In a previous shock tube study, Brabbs, Belles, and Zlatarich[3] deduced the CO_2 dissociation rate at temperatures of 2600°K to 3000°K, from observations of UV emission at a wavelength of 3500 A. Kaskan[4] has shown that in flames this emission, (which is referred to as the CO flame bands), is proportional to the product of CO and O concentrations. This dependence has also been observed at equilibrium conditions in the emission from shock heated gases, and in analyzing the data it was assumed that this proportionality holds during the approach to equilibrium. On comparison of these results with the dissociation rates obtained from the infrared measurements, it was found that the latter are about a factor of four higher than those given by Brabbs et al, although only an indirect comparison was possible because the two temperature ranges do not overlap.

To provide a direct comparison of the dissociation rates determined from the IR and UV measurements, the UV emission at 3500°K was also monitored on each shock wave at these higher temperatures, and a rate constant was determined from the data.

The rate constants for both the UV and IR are given as a function of temperature, and expressed analytically by a least squares fit of the data to both the classical collision theory[5] and an Arrhenius equation.[6] The rate constants determined from the infrared measurements are in agreement with an extrapolation of the rates obtained at the temperatures of 3500°K to 6000°K; the activation energy and the apparent number of degrees of freedom contributing to the dissociation process both appear to decrease with increasing temperature, which is consistent with the increased vibrational excitation and the anticipated effect of the potential energy anharmonicity. The direct comparison of the IR and UV methods confirms the earlier suggestion[1] that the two rates are significantly different and probably refer to different reactions. The report is concluded with a summary of the reaction rates determined by these two methods over a temperature range of 2600°K to 11,000°K.

II.　　EXPERIMENTAL PROCEDURE

Observations

The gas mixtures were heated by shock compression in a 3-inch i.d. uniform bore shock tube which has previously been described in reporting observations of optical properties and reaction rates in CO and CO_2 at high temperatures.[1,7,8] The optical system previously used was modified (Fig. 1) to include an ultraviolet-visible channel so that infrared and either visible or ultraviolet radiation can be monitored simultaneously. In the infrared system, radiation from behind the shock wave is collimated by slits S1, and focused by mirrors M_1-M_3 on the entrance slit of the infrared monochromator. The infrared radiation emerging from the monochromator is focused by mirrors M_4-M_5 on a rapid response InSb detector, whose output signal is amplified, then displayed on an oscilloscope and photographed (Fig. 2a). On the other side of the shock tube, radiation is collimated by slits S2 and directed through the UV-visible monochromator to a photomultiplier tube, whose output is also displayed on an oscilloscope and photographed. (Fig. 2b).

The infrared signal is emission from the $2.7\,\mu$ combination bands of CO_2, which arises from vibrational transitions $(n_1, n_2 + 2^l, n_3+1 \rightarrow n_1, n_2^l, n_3)$ and $(n_1+1, n_2^l, n_3+1 \rightarrow n_1, n_2^l, n_3)$. When the shock wave passes the slit system there is an initial rapid rise in the infrared emission resulting from heating and compression of the test gas. Following this rise there is a
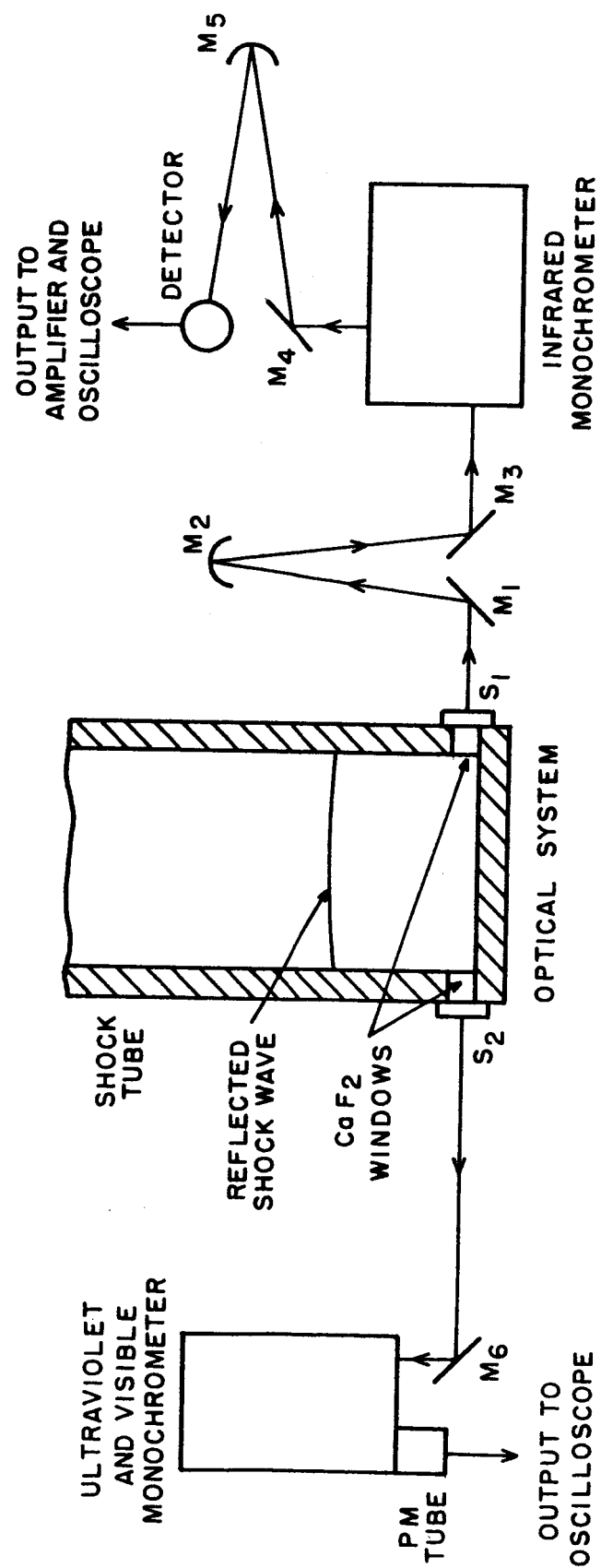
Fig. 1 Optical System

OUTPUT TO AMPLIFIER AND OSCILLOSCOPE

DETECTOR

M5

M4

INFRARED MONOCHROMETER

M2

M3

M1

S1

OPTICAL SYSTEM

SHOCK TUBE

REFLECTED SHOCK WAVE

CaF2 WINDOWS

S2

ULTRAVIOLET AND VISIBLE MONOCHROMETER

M6

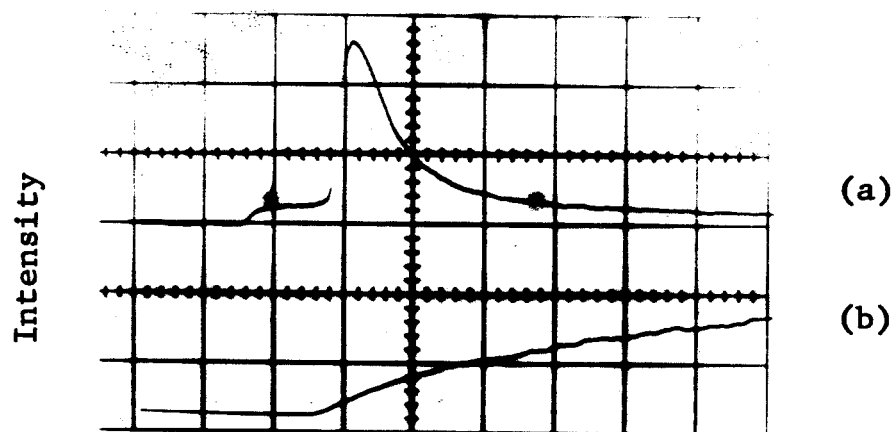PM TUBE

OUTPUT TO OSCILLOSCOPE

Fig. 2 Emission Intensity vs. Time Behind
Shock Wave. (a) IR Emission at 2.9
(b) UV Emission at 3500 A.
Temperature = 8100°K; Pressure = 1 atm
Sweep Speed = 10μ sec/cm.

nearly exponential decay of emission intensity, which indicates
a decrease in the population of excited vibrational states of
CO_2 $(X'\Sigma)$. This decrease is interpreted as CO_2 dissociation.

To obtain the dissociation rate, the relation of the
emission intensity to the CO_2 concentration must be known.
Although the observed radiation could conceivably depend on the
gas temperature and pressure as well as the strength and optical
density of CO_2 and any other infrared active gases that are
present, for the conditions of this experiment the CO_2 concen-
tration is directly proportional to the observed infrared
emission intensity. Since the test gas consisted of one percent
CO_2 in argon, the temperature and pressure of the hot gas depend
primarily on the thermodynamic properties of argon and are not
significantly influenced by the chemical reaction.

The largest CO_2 optical densities in this experiment
were of the order of 0.15 atm-cm. From previous measurements
of the spectral emissivity of these 2.7 M combination bands[2]
it is known that for these optical densities the CO_2 emission
is linear with optical density, and remains linear for optical
densities of almost ten times these values. It was also found
that for temperatures of 2000°K the emission is insensitive
to total pressure above 0.50 atm. This is essentially a statement
that the weak line approximation[9] applies, which implies a
considerable overlapping of rotational lines. At higher
temperatures a larger number of overlapping lines will be excited
so that the emission will continue to be insensitive to changes

in total gas pressure.

The previous measurements of CO_2 dissociation at temperatures of 3500°K to 6000°K were obtained from observations of the 4.3 μ CO_2 band radiation behind incident shock waves. The higher temperatures considered in this report are more easily obtained with reflected shock waves, and at these temperatures it is more convenient to observe the infrared radiation from the 2.7μ combination bands. The advantages of observing the 2.7 μ band emission are that (1) the dissociation products, such as CO, are not strong emitters at these wavelengths, so the emission signal decays more nearly to the zero level, and (2) there is no possibility that the CO_2 will be optically thick at 2.7μ, whereas at 4.3 μ it might be.

The gas purity requirements are more stringent when the observations are made at this wavelength, because the combined integrated absorption of the two fundamental bands of H_2O at 2.66 μ and 2.70 μ is the same order of magnitude as that of the 2.7 μ CO_2 bands. Since the argon and CO_2 were research grade gases that contain negligible amounts of H_2O, any significant amounts of H_2O that are present must be introduced in the gas handling system. Observations of shock waves in pure argon yielded no emission in this wavelength region with the instrument sensitivites used in the CO_2 studies, and observations of the test gas at a wavelength of 6 μ where there is a strong H_2O band also indicated there are no measureable quantities of

H_2O present. From these measurements it appears that the H_2O concentration is no greater than 100 ppm, and may approach the purity of the research grade gas.

The UV spectrophotometer system was used to monitor the CO flame band continuum at a wavelength of 3500 A. In work with flames Kaskan[4] found the intensity of blue emission is proportional to the product of the concentrations $CO('\Sigma)$ $O(^3P)$, and it has been shown that this is also true for detonation waves[10] and shock heated gases.[3] The wavelength of 3500 A was selected because it is near the peak of the emission, and provides a direct comparison with the work of Brabbs et al.[3]

The temperatures were calculated on the assumption that the CO_2 translational, rotational and vibrational equilibrium were complete before significant dissociation occurred, and that the CO_2 dissociation measurements were made before the ionization of argon affected the gas temperature. The characteristic times for CO_2 vibrational relaxation,[10,11] CO_2 dissociation, and argon ionization[12] (Fig. 3) at these temperatures show that above assumptions are reasonable except perhaps for the vibrational relaxation at the highest temperatures. Incomplete vibrational relaxation would not affect the temperature because of the small CO_2 concentration, but would be manifested by a slower dissociation rate if dissociation from excited vibrational levels were important.
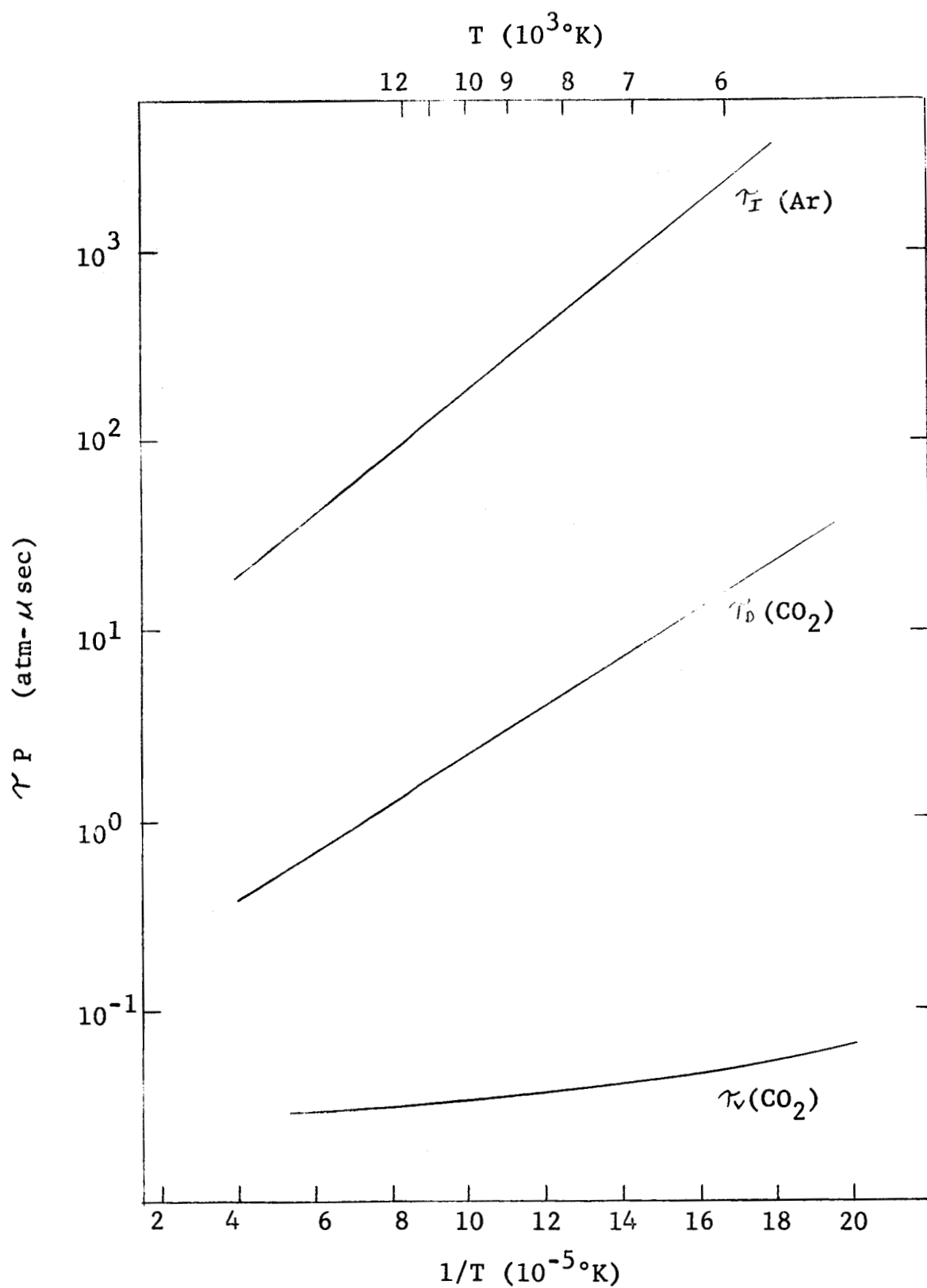
Fig. 3 Characteristic Relaxation Times for (a) Argon
Ionization, τ_I (Ar), (b) CO_2 Dissociation
$\tau_D(CO_2)$, and (c) CO_2 Vibration, $\tau_v(CO_2)$

10

The condition behind reflected shock waves have been investigated by a number of authors, [13-15] and the effect of boundary layer formation and the reflected shock wave velocity on the reaction can be estimated. In inert gases no bifurcation or acceleration is observed, and the reflected shock speed is equal to or slightly less than the theoretical value. Since the test gas was only one percent CO_2 in 99 percent argon, it is expected that the boundary layer effects are small or negligible. In addition, the measurements were made within 10 μ s behind the reflected shock wave, which corresponds to a region of $\leqq$ 10 mm, in which the boundary layer effect will be small. A further indication that this boundary layer effect is not significant is that over the region of 5000°K to 7000°K the dissociation rates determined with reflected shock waves are in agreement with those obtained from the incident shock waves.

III.   DATA ANALYSIS

The reaction being observed is $CO_2 + Ar \rightarrow CO + O + Ar$, which has a dissociation energy of 5.5 eV. At the temperature range of 6000°K to 11,000°K the CO is also dissociating, but the rate of CO dissociation is sufficiently slower than that of CO_2 that the CO concentration is essentially constant in the region just behind the shock wave in which the CO_2 dissociation measurements are made.   The rate of disappearance of CO_2 is described by the first order reaction

$$d \, (CO_2)/dt = - k \, (CO_2) \, (Ar) \qquad (1)$$

and the instantaneous CO_2 concentration is

$$(CO_2) = (CO_2)_o \exp\left[- k \, (Ar) \, t \right] \qquad (2)$$

k is the dissociation rate, $(CO_2)_o$ is the initial CO_2 concentration (Ar) is the argon concentration, and it is assumed that the terms containing products of CO_2 and other atom or molecule concentrations are negligible because of the low concentration of CO_2 and other species. The dissociation rate constant is given by

$$k = \ln 2/(Ar) \, t_{\frac{1}{2}} \qquad (3)$$

where $t_{\frac{1}{2}}$ is the half-life of the dissociation reaction. For the conditions of this experiment, in which the intensity of the

infrared emission is proportional to the CO_2 concentration, the
half-life can be determined from a plot of intensity vs. time
behind the shock wave.

A rate constant is determined from observations of
the UV emission on the assumption that the intensity of this
emission is proportional to the product (CO)(O), and that
initially $(CO) \approx (O)$. If

$$k/(k-k_1) \exp\left[- k_1 (Ar) t\right] \simeq 1 \tag{4}$$

where k_1 is the dissociation rate of CO, the product of CO and
O concentrations is given by

$$I^2 = B(CO)(O) = B\left[(CO_2)_o\right]^2 \left[1 - e^{-k(Ar)t}\right]^2 \tag{5}$$

From measurements of the CO dissociation rate, it is known that
the expression in eqn. 4 is accurate to within two percent for
the conditions of this experiment. The rate constant for the
process is determined from the expression

$$k = \ln 2/2 (Ar) t_2 \tag{6}$$

In this case the characteristic time (t_2) is not the half-life,
but rather a "twice-life", i.e. the time in which the UV intensity
is observed to double.

The rate constants were fit by the method of least squares to the classical collision theory for diatomic molecules, and to an Arrhenius equation, to provide an analytical description of the rate constant as a function of temperature. According to the classical collision theory the rate of change of CO_2 concentration is

$$- \frac{d(CO_2)}{dt} = ZP \ (D/kT)^S/S \ \exp(-D/kT) = k(CO_2)(Ar) \quad (7)$$

where Z is the collision frequency, the steric factor P is the probability that a collision with sufficient energy will produce a dissociation, D is the dissociation energy, k is the Boltzmann constant, T is the absolute temperature and S is a factor that gives the number of transverse translational and internal energy degrees of freedom that contribute energy to the dissociation process. Using the collision frequency from the kinetic theory the rate constant becomes

$$k = (P \ r^2/S \ )(8\pi kT/m)^{\frac{1}{2}} \ (D/kT)^S \ \exp(- \ D/kT) \quad (8)$$

where r is the effective collision radius and m is the reduced mass of the CO_2-Ar system. Since the choice of the steric factor P, the collision radius r, and the value of S are uncertain, the rate constants were fit to the equation

$$k = C \ (D/kT)^n \ \exp(- \ D/kT) \quad (9)$$

to provide the constants C and n, which were then used to calculate S and P.

The factor S is a measure of the degrees of freedom, other than translation along the line of centers, that contribute to the dissociation process. The maximum value of S can be calculated by considering the number of atoms involved in the collision; for a CO_2-Ar collision, in which angular momentum is conserved, the maximum value is five. Even if this theory were a perfect description of the reaction in other respects, one would expect this value of S to become < 5 as temperature is increased, because the theory is developed on the assumption that the vibration can be described by a harmonic oscillator. As temperature increases, the effects of anharmonicity are such that less vibrational energy is available than in the harmonic oscillator approximation.

There are a number of assumptions inherent in the attempt to describe this reaction with the classical collision theory. The expression for the rate constant is derived for collisions involving a diatomic molecule, so that in this application CO and O take the place of two atoms. While this is a reasonable assumption at lower temperatures, it might be questionable as temperatures are reached at which CO dissociation is significant. However, since the measurements of CO_2 dissociation were made just behind the shock wave before appreciable amounts of CO are dissociated, the physical process is not greatly different at these higher temperatures.

The dissociation rate data were fit to Arrhenius equation of the form

$$k = C \, T^{\frac{1}{2}} \exp(- \, Q/kT) \tag{10}$$

to determine an activation energy (Q) for the reaction. It is expected that the activation energy will be less than the CO bond dissociation energy of 5.5 eV, because dissociation will occur from excited vibrational levels. At these higher temperatures it might also be expected that the activation energy will be less than the 3.24 eV determined for this reaction at 3500°K to 6000°K.

IV.   RESULTS

The dissociation rate constants determined from the infrared measurements are shown in Fig. 4. The least squares fit to the classical collision theory (eqn. 9) and the Arrhenius equation (eqn. 10) yield the expressions (in cm^3/particle-sec)

$$k = 8.95 \times 10^{-13} \ (D/kT)^{3.21} \ \exp(- D/kT) \qquad (11)$$

and

$$k = 1.92 \times 10^{-13} \ T^{\frac{1}{2}} \ \exp(- 2.96 \ eV/kT) \qquad (12)$$

respectively.

According to the classical collision theory the number of transverse translational and internal energy degrees of freedom that contribute to the dissociation process is $S = n + \frac{1}{2} = 3.71$ for this temperature range. For a CO_2-Ar collision in which angular momentum is conserved, the value of S should be ≤ 5, so this value of $S = 3.71$ appears to be physically reasonable. There are several plausible explanations for the fact that this value of S is less than the $S = 4.88$ obtained for temperatures of 3500°K to 6000°K. As mentioned above, there is actually less energy available at higher temperatures than this theory implies, because the vibrationally excited levels are not accurately represented by a harmonic oscillator. Furthermore, the vibrational relaxation may not
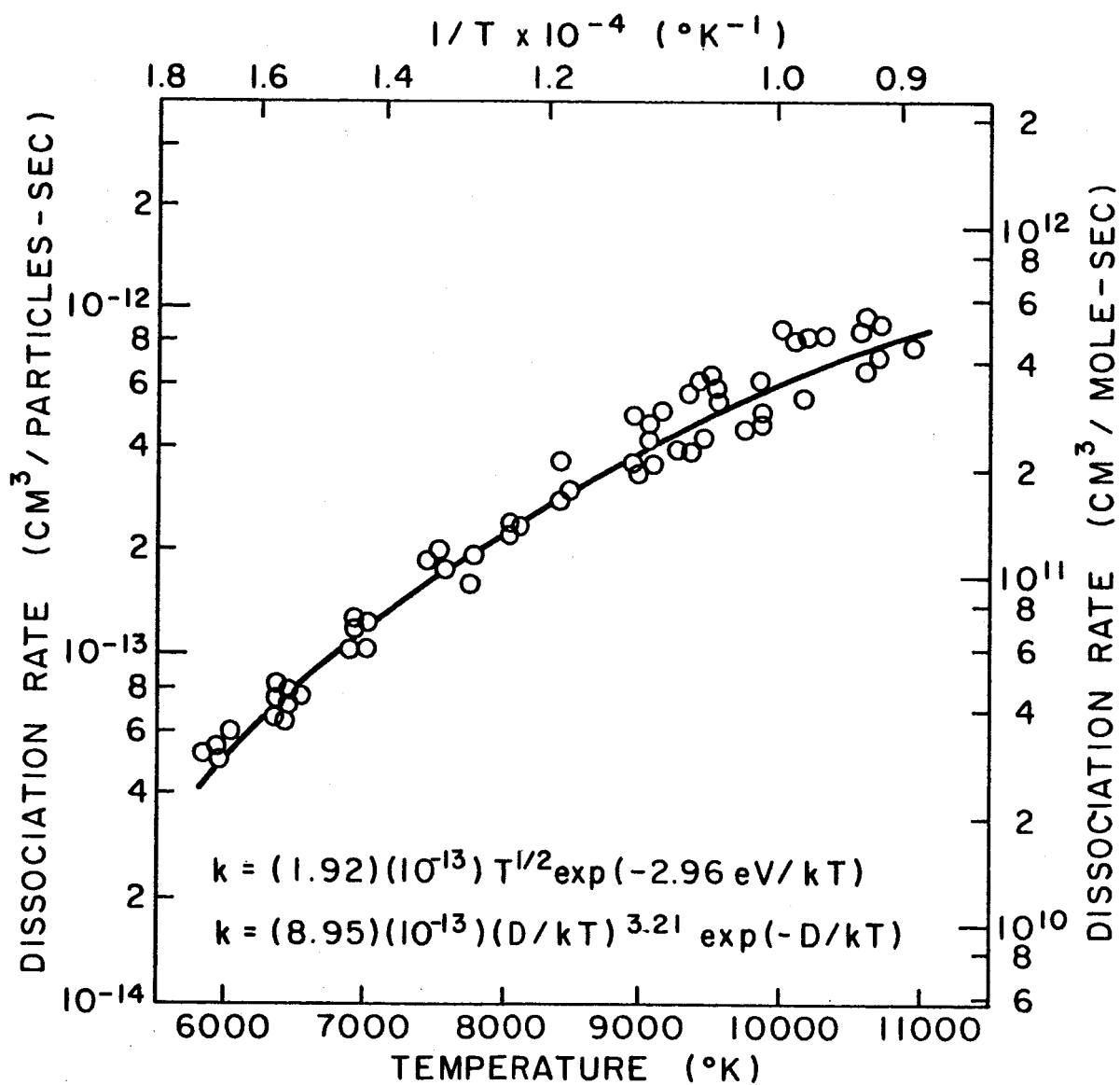
Fig. 4 CO_2 Dissociation Rate vs. Temperature From Infrared Emission. One Percent CO_2 in Argon.

The curve fits are given by:

$$k = (1.92)(10^{-13}) T^{1/2} \exp(-2.96 \, eV/kT)$$

$$k = (8.95)(10^{-13})(D/kT)^{3.21} \exp(-D/kT)$$

be complete before dissociation occurs so that even the total vibrational energy of anharmonic oscillator will not be available for the dissociation process. The steric factor obtained from the data is 2×10^{-3} if a collision radius from viscosity measurements is used; this value is somewhat lower than the values of ~ 1 to 10^{-2} that would be expected if the theory is applicable, which suggests that the physical picture is not correct.

Thus an interpretation of the CO_2 dissociation rate constants in terms of the classical collision theory yields the same conclusion that was deduced from the measurements at lower temperatures. Although the value of S appears to be physically reasonable, the steric factor is sufficiently low that the applicability of the theory is, at best, questionable. While the physical picture of the collision process should not be overemphasized, the theory will suffice to provide an accurate analytical description of the disappearance of CO_2 behind shock waves.

As expected, the activation of 2.96 eV is considerably less than the 5.5 eV for the CO_2 bond energy, and is also lower than the 3.24 eV activation energy obtained at temperatures of 3500°K to 6000°K. These results are consistent with the theories that suggest dissociation occurs from excited vibrational levels, but no attempt is made to determine which of these models is the best description of the process.

The dissociation rates determined from the UV radiation are given as a function of temperature in Fig. 5. The least squares fit of this data to the classical collision theory and the Arrhenius equation yields the expressions (in cm^3/particles-sec)

$$k = 2.89 \times 10^{-12} (D/kT)^{2.04} \exp(- D/kT) \qquad (13)$$

$$k = 1.61 \times 10^{-13} T^{\frac{1}{2}} \exp (- 3.68 \text{ eV}/kT) \qquad (14)$$

respectively. The scatter of the data based on UV measurements is greater than that of the infrared but the accuracy is still sufficient to provide a comparison. The primary reason for this scatter is that the measurement is obtained from a slowly rising oscilloscope trace, while the infrared measurement is on a rapidly decreasing signal.

A comparison of these measurements with the rates determined from the infrared radiation suggests that two different reactions are being observed. The rate constants from the infrared observations are about a factor of three larger than those determined from the UV measurements. This result might have been anticipated from the previous comparison of our infrared observations with the rate constants obtained from UV measurements of Brabbs et al,[3] but the simultaneous measurement of these rates on the same shock wave provides a more satisfactory comparison. Considering the range of temperatures involved, the activation energy of 3.68 eV is in

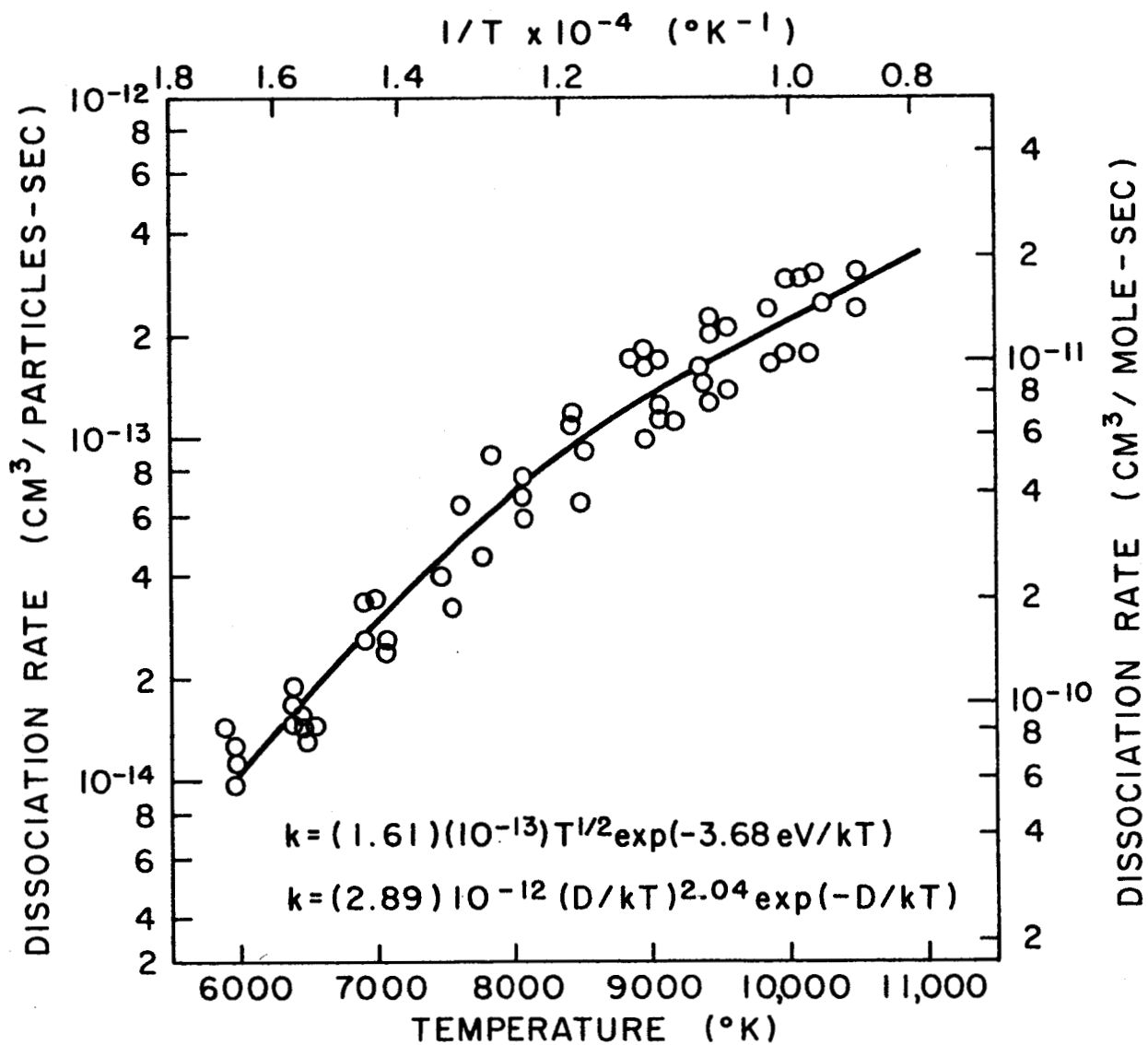Fig. 5   CO$_2$ Dissociation Rate vs. Temperature From Ultraviolet Emission.   One Percent CO$_2$ in Argon.

The figure shows the following equations:

$$k = (1.61)(10^{-13}) T^{1/2} \exp(-3.68\,eV/kT)$$

$$k = (2.89)\,10^{-12}\,(D/kT)^{2.04} \exp(-D/kT)$$

good agreement with the 3.73 eV obtained at temperatures of about 3000°K, and is considerably higher than the 2.96 eV from the infrared measurements. Since it is believed that the rate obtained from the UV observations does not represent the CO_2 dissociation rate, no attempt has been made to interpret the constants obtained in the classical collision equation.

A summary of shock tube measurements of CO_2 dissociation for temperatures from 2600°K to 11,000°K is presented in Fig. 6, in which the Arrhenius equations are plotted for the data presented in this report, the infrared measurements for temperatures of 3500°K to 6000°K,[1] and the rates determined at 2600°K to 3000°K.[3] The solid lines indicate the temperature range over which data was obtained for each curve, and the dotted lines are extrapolations to other temperatures. The rate constants determined from the two sets of infrared measurements are in agreement, and are higher than the UV measurements by about a factor of three. Considering the temperature range over which the extrapolation is made, the UV measurements made in these experiments are in fair agreement with the lower temperature results of Brabbs et al.

The activation energies, steric factors and values of S for these measurements are given in Table 1. The activation energies from the infrared measurements are consistent with the increased vibrational excitation at the higher temperatures, and the activation energies obtained from the separate UV
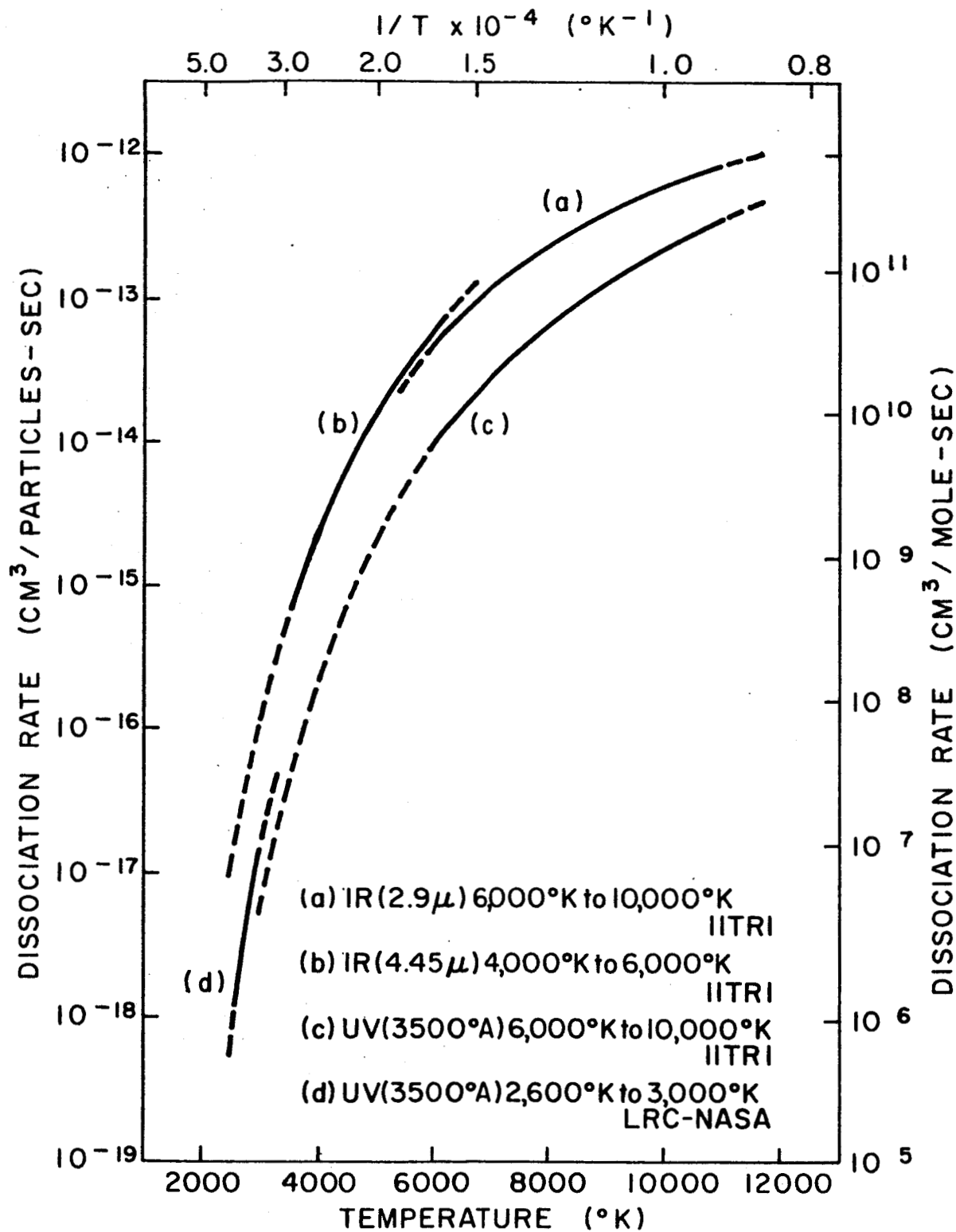
Fig. 6   Summary of CO_2 Dissociation Measurements.

TABLE I

ACTIVATION ENERGY, STERIC FACTOR, AND ACTIVE DEGREES
OF FREEDOM IN CO_2 DISSOCIATION

T(°K)	Q(eV)		S		P	
	IR	UV	IR	UV	IR	UV
2600-3000[*] (Reflected Shock)	---	3.73	---	7.11	---	7×10^{-8}
4000-6000 (Incident Shock)	3.24	---	4.88	---	2.2×10^{-3}	---
6000-10,000 (Reflected Shock)	2.96	3.68	3.71	2.54	1.4×10^{-3}	2.5×10^{-3}

[*]Lewis Research Center, NASA

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measurements appear to be in agreement. The difference in these activation energies suggests that the UV and infrared radiation represent two different reactions. The values of S determined from the infrared measurements are physically reasonable, and consistent with the theories that suggest dissociation occurs preferentially from upper vibrational levels, but the low values of steric factors suggest the theory is not applicable to this set of observations.

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